MANUFACTURE OF CALCIUM CYANAMIDE BY THE USE OF NITROGEN OBTAINED FROM COMBUSTION GASES

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THE MANUFACTURE OF CALCIUM CYANAMIDE BY THE USE OF NITROGEN OBTAINED FROM COMBUSTION GASES.

A THESIS

Presented by

T. CECIL FORD and JOSEPH L. DUNHAM

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THE MANUFACTURE OF CALCIUM CYANAMIDE BY THE USE OF NITROGEN OBTAINED FROM COMBUSTION GASES.

Introduction.

Nitrogen is one of the most useful elements when in the combined state and one of the most useless when in the free state. It is a constituent of nearly all foods and is found in all plants. Vegetation can not exist without a sufficient supply of nitrogen in the soil. This supply is becoming depleted in many parts of the globe and artificial fertilizers have to be applied to the soil to make it fertile. At present, most of the nitrogenous fertilizers come from Chili salt petre and ammonium sulphate. The salt petre occurs in natural beds in the arid regions of Chili. This supply is far from inexhaustible, especially with a yearly consumption of over a million and a half tons and it has been estimated

that the beds will be exhausted by 1923. They may last a few years longer than that but nevertheless they will soon be gone. When that time comes some other body high in nitrogen must be found. The ammonium sulphate can not be used to supply this want, as all the sulphate comes from the coke ovens and they are now producing practically all the ammonia which can be obtained from the coal. Because of this scarcity of nitrogen compounds it is necessary to look for some place where nitrogen can be obtained abundantly. The air is our largest source of nitrogen, therefore it is to this that the chemist turns.

EARLY ATTEMPTS TO FIX ATMOSPHERIC NITROGEN.

The fixation of atmospheric nitrogen has long been one of the great problems of the research chemist. This problem, despite its many difficulties, has held the attention of chemists for over half a century. One of the first methods which was put on a commercial scale was begun in France in 1840. Potassium ferro-cyanide was made by the use of atmospheric nitrogen. At one time the output of the factory was nearly a ton per day. The plant proved unprofitable, however, and was soon shut down.

More recently experimenters have devised a method for combining oxygen and nitrogen by means of an electric arc. Air is drawn through an electric arc and the gases of combustion are absorbed by water forming nitric acid. This method was very inefficient because only a small portion of the air drawn through the arc was converted into nitric oxide. In the later forms of this apparatus, a tube with many needle-like projec-

tions on its inner surface is used as one electrode. The other electrode is smaller and has similar projections on its outer surface. The latter electrode passes through the former and has a revolving motion. The revolving of the inner electrode causes an almost continuous discharge throughout the cylinder. The gases drawn through this form of arc carry much more nitric oxide than those obtained by the earlier method; but the process is still very inefficient. Under the most favorable conditions only a very small percent of the nitrogen can be oxidized, usually under five percent. In a still later development of the process a radioactive substance is put into the arc and the gases which pass through are quickly cooled. None of these methods, however, has shown an efficiency high enough to warrant any faith in the process.

A considerable amount of work has been done to obtain a combination of nitrogen with

some metal to form a nitride. It was noticed that when certain elements, as silicon and boron, were heated in an atmosphere of nitrogen they absorbed the nitrogen forming nitrides. These nitrides could then be decomposed by steam into ammonia. The great difficulty with this process was the reconverting of the boron compound, which resulted from the action of the steam, into a substance which would again unite with nitrogen. Various metals and compounds were tried but in each case the same difficulty was encountered and it has not yet been overcome.

Another group of experimenters have worked along somewhat similar lines. They have tried to combine nitrogen either with hydrogen, to form ammonia, or with some compound producing an ammonium salt from which ammonia might be liberated. Attempts have been made to combine nitrogen and hydrogen in an electric arc but the results obtained have not been sufficiently sat-

isfactory to warrant making a statement in regard to the process. By far the greatest advance has been made in the manufacture of calcium cyanamide. This substance is now being manufactured in Norway from calcium carbide and nitrogen under patents held by Adolph Frank and Nikodem Coro. By their process a body having from fourteen to twenty percent nitrogen can be obtained.

Before going further into the process of the manufacture of calcium cyanamide it may be well to tell something of its composition and use. As manufactured by Dr. Frank it is a black, stable powder and has approximately the following analysis:

Pure calcium cyanamide, $CaCN_2$	57.0%
Free carbon,	14.0"
Caustic lime,	21.0"
Silica, SiO_2	2.5"
Iron oxide, Fe_2O_3	4.0"

Sulphur,	Trace
Phosphorus,	"
Carbon dioxide,	"

A sample of good cyanamide should contain twenty percent of nitrogen. The free carbon imparts the black color to the mass. When it is put into hot water it decomposes into lime and a complicated polimerization body called dicyandiamide. If steam, at a temperature of 160° to 180° C, be passed over cyanamide it decomposes into ammonia quantitatively. In aquaous solution with acids it forms many interesting organic bodies, among which is urea. When cyanamide is fused with some salt of the alkali metals such as sodium carbonate or chloride it forms the alkali cyanide together with calcium cyanide, and the products resulting from the decomposition of the salt used. By this reaction all the nitrogen can be converted into cyanide nitrogen.

PRACTICAL USES OF CALCIUM CYANAMIDE.

Calcium cyanamide can be used in a great many ways, the most important of which is as a fertilizer. It must not be used on acid humus soils nor on sandy soils which are only slightly active or are acid. A light, clayish, sand soil is too light to give good results. In order to secure good results the soil must be rather moist and preferably of a lime formation. Any kind of soil except those mentioned above is much benefited by the application of cyanamide. The cyanamide should be mixed with about twice its weight of dry earth before applying and then should be worked well into the ground before sowing the seed. It should be from three to five inches below the surface and should never be applied as a top dressing nor after the seeds have started to germinate. Its action as a fertilizer compares very favorably with that of ammonium sulphate and Chili salt petre. Some agriculturists have declared

against its use but the general consensus of opinion seems to be that it is as good as either of the fertilizers just named, for the growth of potatoes, oats, barley and wheat.

Calcium cyanamide contains free carbon and lime. In the presence of moisture, as in the soil, the lime is slacked. The slacked lime then reacts with the cyanamide to form a complicated body which decomposes in the presence of water into the cyanamide acid. Under the influence of heat or carbon dioxide gas, this body polimerizes into a body of twice its molecular weight, called dicyandiamide. The equations representing the reactions are as follows:

$$CaO + H_2O = Ca(OH)_2$$

$$Ca(OH)_2 + CaCN_2 = C\begin{pmatrix} N\text{-}Ca\text{-}OH \\ N\text{-}Ca\text{-}OH \end{pmatrix}$$

$$C\begin{pmatrix} N\text{-}Ca\text{-}OH \\ N\text{-}Ca\text{-}OH \end{pmatrix} + 2H_2O = C\begin{pmatrix} N\text{-}H \\ N\text{-}H \end{pmatrix} + 2Ca(OH)_2$$

Practical Uses of Calcium Cyanamide.

$$2\ C \begin{pmatrix} N\text{-}H \\ \\ N\text{-}H \end{pmatrix} \text{(heated)} = C_2(NH)_4$$

The final body formed is very helpful to the growth of young plants. As the plants become older they are able to make use of the undecomposed cyanamide, which was of no value to the very young plants.

If the cyanamide is to be used as a fertilizer it should contain at least ten percent nitrogen.

Another important use of cyanamide is in the manufacture of ammonia and ammonia derivatives. Steam under pressure of from six to ten atmospheres liberates ammonia quantitatively according to the equation:

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

This reaction is made use of to a large extent. In carrying out the process, the cyanamide is laid on shelves in a steel cylinder and steam passed up through it, carrying off the am-

monia. This ammonia is very pure and free from empryheuma. Ammonia water can be obtained by bubbling the gas through water. By absorbing the ammonia in sulphuric acid a good grade of ammonium sulphate can be made. This sulphate may be used as fertilizer where it is not desirable to introduce lime into the soil.

Dicyandiamide is a compound much used in the manufacture of analine dyes and also in gunpowder. The dicyandiamide is prepared according to the equation:

$$2CaCN_2 + 4\ H_2O = 2\ Ca(OH) + (CNHH)$$

By suitable leaching with water and crystallization the dicyandiamide separates out in beautiful white crystals. This body has sixty-six and two-thirds percent nitrogen and because of this it is especially valuable in explosives. The nitrogen is liberated on explosion but it reacts very little and does not corrode the gun barrel to any extent. It does not heat up as many

of the gases liberated and so it keeps the barrel cooler and thus lengthens its life. This is of great advantage in powder used in ordnance, such as cordite and filite. The flame is also diminished. In all probability the preparation of dicyandiamide will become of considerable importance as soon as calcium cyanamide can be made on a large scale.

Sodium and potassium cyanides can be made by fusing cyanamide with their chlorides. The reaction is represented by the following equation:

$$C+CaN_2+NaCl = CaCN+NaCN+Cl.$$

The free carbon which is always in the commercial cyanamide supplies the necessary carbon. An excess of salt is always employed and the resulting mixture contains from twenty-two to twenty-three per cent sodium cyanide. This mixture is often sold directly to the gold metallur-

gist as "sodium cyanide substitute" or "Surrogat." If a pure product is desired, it is reworked and made into chemically pure sodium cyanide. This process was devised by Frendenburg and will soon be put into operation on a commercial basis, near Berlin, Germany.

Calcium Cyanamide has found a new use as a hardening material for iron and steel. The cyanamide contains free carbon and it is its ability to give up this carbon to the heated steel which makes it valuable. The impregnation of the steel is deep and very uniform and takes place at a temperature where all other substances produce an uneven hardening effect. This makes it a very valuable material in the manufacture of tool steel. It is already known to the trade as "Ferrodur" and it will probably increase in popularity as time goes on.

Urea is now being manufactured in a

small factory by treating cyanamide with suitable acids. A solution of urea is thus obtained from which the pure product may be easily crystallized.

The above are some of the more common uses to which calcium cyanamide may be put and its usefulness will undoubtedly increase as it becomes a more common article of trade.

Early Work with Calcium Cyanamide.

The first record of combining nitrogen in a simple compound comes from Fownes and Young. They devised a method which was later carried out with fair success by Bunsen sometime during the last century. It consisted in passing nitrogen over carbon and the alkalies or the alkaline earths with the formation of cyanide which could later be treated for ammonia. The practical results from these experiments were inconsiderable owing to the high temperature which was required and which was very difficult for them to obtain.

Early Work with Calcium Cyanamide.

Later the dynamo was invented and it opened up a hitherto unreached range of temperature. Carbide was produced in the electric furnace by Moisson who then attempted to obtain an absorption of nitrogen by the carbide. He obtained a poor yield when steam was admitted with the gas and no yield at all with dry nitrogen. In 1895 Adelph Frank succeeded in fixing nitrogen in calcium carbide by the use of a small amount of sodium carbonate. A cyanide was formed but the yield was poor. He found that by substituting barium for calcium carbide the yield was increased and the combining temperature reduced to 700° to 800° C. They found that the resulting product was thirty percent cyanide and forty-five percent cyanide but that by fusing with potassium carbonate, the whole could be changed to potassium cyanide, the body which they desired.

Calcium carbide was so much cheaper than the barium compound that they tried other

experiments with it. They found that without using any flux, the reaction proceeded so as to form cyanamide which could be changed like the barium compound into potassium cyanide. When the Boer war stopped the mining of gold in South Africa the price of the cyanide fell and they had to cheapen their process or find some new use for the cyanide. Then they used the calcium carbide altogether, and they soon found that it could be made with enough nitrogen to be a good fertilizer.

Since Frank's discovery there has been much work done to cheapen the cost of production and to find new methods for the manufacture of cyanamide. These methods naturally fall into two great divisions. The first consists of the manufacture of cyanamide from carbide and follows the general methods employed by Dr. Frank. The second starts with lime and coke and consists in forming the cyanamide directly instead of first forming the intermediate product, the carbide.

EXPERIMENTS USING THE ELECTRIC FURNACE.

This method has been worked out chiefly by the Siemens and Halske Co.

The second method is the one we tried first and so it will be described first. Lime and coke can not be combined at any temperature below that of the electric furnace. The process consists in thoroughly mixing powdered or crushed lime and coke and then heating the mixture in an electric furnace in an atmosphere of nitrogen. In some cases a catalytic agent is used, although not always. The nature of the catalyzer varies considerably.

Experiments Using the Electric Furnace.

Before describing our various trials a description of the furnace will be given. The furnace was set up by us and had to be, at least partially, torn down every time a charge was put in or taken out,

Experiments Using the Electric Furnace.

The furnace was of the vertical arc type and consisted of two carbon electrodes 4½" x 4½" x 24" surrounded by a wall of magnesia brick, which rested on hollow building tiles placed on end. The electrodes were connected to the external circuit by means of aluminum plates 3/8" x 4½" x 12" bolted to opposite sides of one end of the electrode. One electrode was set on end and the tiles set up around it reaching to within five inches of the top. A space of about two inches on each side was left between the electrode and the tile. The bricks used were made of magnesite and were capable of withstanding any temperature we were able to obtain. The greatest difficulty was the cracking and crumbling of the bricks under the intense heat. The bricks were built up closely about the electrode from the top of the tiles forming a four inch wall. These walls were extended eighteen inches above the top of the lower electrode leaving a space 4½" x 4½". The upper electrode was supported by a wire suspended from

a pulley so that the height of the electrode might be adjusted. After the first heat a one inch hole was drilled from one side and six inches from the top, nearly through the lower electrode. From the top nine quarter inch holes were drilled into the larger hole, into which a one inch pipe was screwed. This pipe was connected to a blower so arranged that either nitrogen or air could be blown into the furnace. No arrangement was made for the escaping gases other than the cracks between the bricks and the space between them and the electrode.

The purpose of the first heat we ran was principally to become familiar with the apparatus and method of proceedure but it is interesting because we obtained nearly as good a nitrogen absorption as in any of the other heats. We had a charge of ten pounds of lime and coke thoroughly mixed and pulverized. The proportions of lime to coke were as 56:24 because we wished the reaction to proceed as follows:

$$CaO+2C = CaCN_2+CO$$

Experiments Using the Electric Furnace.

In this heat both electrodes were solid and no gas was blown into the mass. The lower electrode was covered with small pieces of coke and then the mixture was put into the furnace. An electric light carbon extended up through the mixture and connected the electrodes. Small pieces of coke were also laid between the mixture and the upper electrode. Alternating current at a pressure of fifty volts was used - the current at the start was one hundred amperes. This passed through the lamp carbon and heated the central portion of the mixture. As the mass became heated the resistance decreased and the current increased. The mixture had this peculiarity that it only conducted current at high temperatures. As the mass was heated up more current was turned on until about three hundred amperes were sent through the arc. The charge shrunk as it was heated and the upper electrode had to be lowered. As soon as the mixture was thoroughly heated carbon monoxide was given

off coming out through the crevices of the brick, burning with an intense flame. The gas first came from the upper part of the charge but as the reaction proceeded the gas came from lower levels. The current was sent through the furnace for about three hours after which it was turned off and the furnace allowed to cool until the next day. The mass had fused and occupied only about one-third of its original volume. It smelled strongly of acetylene and was very hard. The temperature of the furnace had been such that the bricks which surrounded the zone of the heated carbide were broken.

This fused mass was removed and pulverized, then analyzed for nitrogen. The customary Kieldahl method of analysis except that about twenty cubic centimeters of water were added with the sulphuric acid in order to decompose the carbide into lime and acetylene. Without the addition of the water the time of digestion was greatly lengthened. The analysis showed 1.25 percent

nitrogen.

Before the second heat holes had been bored in the lower electrode and the blower connected as described above. The charge consisted of equal parts of lime and coke. This excess coke was added because we intended to blow air through the mass and we wished to allow for whatever coke might be burned. The lime and coke had all been passed through a #4 sieve and had been retained by a #8. The mixture was charged the same as before and a low current used until the furnace was hot. From 300 to 400 amperes were sent through the furnace for fifty minutes after it became hot. Air was blown through the furnace most of the time. After the furnace had cooled it was found that the lower part had fused into a solid cake while the upper part was still in small lumps. Analyses were made of the fused and powdered portion for nitrogen but the percentage in each was very low, averaging 1.35%.

Experiments Using the Electric Furnace.

The charge for the third heat was as follows:

Coke,	23.7 %
Air slacked lime,	71.0 "
Potassium Carbonate,	5.23"

The coke and lime passed through a #4 sieve and were retained by a #8. The potassium carbonate was used as a catalyzer. The charge was heated as usual and then nitrogen was blown into the furnace. The furnace was kept at a high temperature for three hours. When the mass had cooled it was found that it had all fused and stopped up all the gas holes, except one, in the electrode. That one was greatly enlarged and the gas evidently had formed a path so that it blew out the side of the furnace near the bottom. Practically none of the gas had been absorbed by the fused mass as an analysis showed about the same nitrogen content as the preceding heats. These results offered no encouragement to this

method so we decided to try another.

In actual practice cyanamide is made in the electric furnace by heating carbide in an atmosphere of nitrogen under a considerable pressure for some time. We had no facilities for obtaining a high gas pressure or for holding the gas in the furnace so we did not try this method. This process is now in use in Odda, Norway, where 196 furnaces turn out 12500 tons of cyanamide per year. Their product runs from 20 to 22% nitrogen. These furnaces take a charge of 300 kilograms carbide and are heated to about 900° C. It takes forty-five hours, including the time for cooling, to run a charge.

Experiments Using the Bomb.

Our next experiments were with calcium carbide and nitrogen heated in a bomb in a muffle furnace. The bomb consisted of a piece of 2½" pipe about 6" long with a nipple on either end

into which plugs were fitted. Both plugs were tapped and in one a half-inch pipe 18" long was fitted and in the other a plug. The over-all length of the bomb except for the extended pipe was 8". A rubber hose was fastened to the end of the pipe and connected it to a water-sealed gas tank. The charge was put in the bomb, the small plug removed and nitrogen passed through to drive out the air. The plug was covered with white lead and again screwed tightly in place. The first bomb was not painted and it soon oxidized and broke. The second one was painted with a liquid carbon paint and it withstood the oxidizing action of the muffle very well.

In the first experiment we filled the bomb half full of calcium carbide which had passed a #6 sieve. The air was expelled as described above and the bomb placed in the muffle and the opening of the furnace closed with a sheet of asbestos. The pressure of the nitrogen in the bomb

was about 18 inches of water. The bomb was heated to from 1000° to 1100° C for six hours.

The analysis of the gas was as follows:

CO_2 . . . . . 0.8%

O . . . . . 0.6"

CO . . . . . 9.6"

N . . . . . .89.0"

The carbon monoxide is entirely too high. The oxygen present probably was due to some air being drawn into the system between the burner and the tank.

The materials came out of the bomb in practically the same condition in which they were put in. On analysis it showed less than two per cent nitrogen. The probable cause for this was the impurity of the gas and the low pressure. The mass had not caked in the bomb, probably because there was very little powdered carbide present. It was all in fair-sized pieces which would not adhere to each other. The carbon monoxide caused

a change of the carbide into lime and carbon which formed a coating over the pieces and stopped all further action.

In the next heat we mixed the carbide with 5% of potassium carbonate. The charge was pulverized and thoroughly mixed. Only one-half pound was used in order that there might be more gas space and a better chance for coming in contact with the carbide. The charge was heated to 900° - 1000° C for four hours. The gas analysis was as follows:

CO_2	5. %
CO.	7.5"
N	87.5"

The bomb was turned at intervals of about fifteen minutes in order to expose new surface of the carbide to the gas. The pressure was the same as before.

Upon attempting to remove the charge it was found to be caked and hard to get out. There

probably was a coating of lime on the surface but we could not open the bomb to find out. An analysis showed no more nitrogen than previously obtained.

Our last heat was run with calcium fluoride as a catalyzer. One experimenter had tried this catalytic agent and reported very favorable results, in an experimental way. The carbide was crushed to pass a #10 sieve and was mixed with five percent calcium fluoride. The gas analysis was as follows:

CO_2	4.8%
CO	1.6"
N	93.6"

Before sending it into the bomb it was passed through solutions of cuprous chloride and caustic potash. No analysis was made of the gas after it passed through these wash bottles, but as it went through very slowly it was probably pure nitrogen. The gas was under a pressure of

eighteen inches of water. The temperature was kept at about 950° C for six hours. The gas bubbled through the solution very slowly so it was apparent there was very little absorption taking place. After the bomb had cooled the charge was removed. In appearance it resembled the first charge as it did not cake or stick together. In water it produced a violent evolution of acetylene. The nitrogen content was again negligible. The cause of this failure was probably insufficicent gas pressure and also too short a duration of the heating. We should have a pressure of two atmospheres or more in order to obtain a good absorption, as the speed of absorption varies directly with the pressure of the gas. This was the only heat where we had good nitrogen.

Method of Obtaining Nitrogen.

Before it is possible to make the cyanamide there must be a good supply of practically

pure nitrogen. Air can not be used because of the oxygen it contains. Ordinary combustion gases can not be used because they contain considerable quantities of carbon monoxide and carbon dioxide. The carbon dioxide is not particularly harmful at low temperatures but at any temperature above 1025° C the dioxide tends to decompose into monoxide. Carbon monoxide is very harmful in the retort because it reacts with the carbide to form lime and coke, thus

$$CaC_2 - CO - CaO - 3\ C.$$

The lime forms a coating over the surface of the carbide and prevents any further action. This reaction caused us more difficulty than any other. Because of the harmful effects of the carbon monoxide producer gas can not be used. Practically no impurities are permissible in the nitrogen.

There are two methods in general use for the production of nitrogen. One depends upon the affinity of copper for oxygen and the other is based upon the different boiling points of nitrogen

and oxygen.

In the first process air is passed through a tube containing red hot copper filings. The copper is oxidized and the nitrogen passes on. The copper oxide is then treated with a current of some reducing gas and reconverted into copper. Where this method is employed the gas, after losing its oxygen, goes directly to the furnace containing the carbide.

The second process depends upon a discovery made by Linde. When air under pressure is allowed to expand suddenly, it cools. If the expansion can be accomplished rapidly the temperature will be greatly lowered and this can be used to cool off the gas near the outlet. The process is carried out as follows: -air is compressed and allowed to flow through a very small opening. In escaping it expands rapidly and cools off the surrounding air. This lowers the temperature to a very marked extent. By two or three repetitions

of this process a temperature of 200° C below zero can be obtained. This is below the boiling point of air and so all the air in the apparatus is liquified. The liquid air can be prepared on a commercial basis. The liquid air is then put into a still somewhat similar to an alcohol still and fractionally distilled. Nitrogen boils at a lower temperature than oxygen and so it evaporates first and is collected in a condenser.

These are the two methods now employed to obtain pure nitrogen. They both yield good products but the cost of production is high, making the price of cyanamide, made from nitrogen thus prepared, excessive. If a cheaper method of making pure nitrogen can be found it would certainly make the preparation of cyanamide a commercial success.

In our experiments we used a new method, for preparing nitrogen, which on the whole was satisfactory. There are a few necessary improvements which could easily be made. The method is

due to Mr. O. P. Hurford, the operation and technical details worked out by Professor Harry McCormack.

The method consists of the complete combustion of some fuel, as oil and the absorption of the carbon dioxide by lime and lime water. The actual operation of the nitrogen plant is as follows:- Crude oil is put into one tank and water into another. The tanks are connected above the level of the liquids to a compression pump. A pressure of 25 pounds to the square inch is applied to the liquids. This forces the water into a ring which surrounds a burner of special design. The ring must be heated enough to vaporize part of the water in it. Oil and steam are then admitted to the burner, and by opening a conical valve they are forced out the steam atomizing the oil so that it vaporizes readily when it is sprayed into the fire box. The fire box is made of brick and directly in front of the hole through which

the oil and steam enter there is a brick wall in front of which are pieces of coke. The hot brick and coke vaporize and ignite the oil and the flame plays back on the water ring and vaporizes the water. The gases of combustion are drawn from the fire box, by means of a suction pump, through a set of washers and scrubbers.

The washer consists of an air-tight box fitted with baffle plates between which coke is placed and water flows down slowly over the coke. The baffle plates are so arranged that the gases go over the top of one and under the next and so on. This washer cools the gases and removes some of the carbon dioxide.

The gases next pass through a lime water scrubber which consists of an air-tight box partially filled with lime water. Extending down from the top are several wooden partitions which extend down into the liquid about one-half inch. The gas enters through a number of small holes in a pipe which is immersed in the water. The scrub-

ber we used was not designed properly. In it each partition extended down the same distance. Then with the pressure constant all the water will be forced into the last compartment, because in each previous section the gas will force the water to the level of the partition under which it escapes and as the partitions were all at the same level the water will all be forced into the last section. This action may not go to completion but there is a tendency in that direction and it should be avoided. With the water at the lower level of all the boards there will be practically no solution for the gas to bubble through. By dipping the first section several inches into the water the next an inch less and continuing thus until the last partition may be above the surface of the water before there is any pressure introduced, a more efficient scrubber may be built for the same cost. In this case the gas will have to bubble through a layer of the solution equal to vertical

distance between the bottoms of the partitions.

After the gas passes through the lime water scrubber it enters a dry lime scrubber. This is a metal cylindrical tank filled with large pieces of unslacked lime. This should remove the last trace of CO_2 but we never made any runs in which the nitrogen contained less than 2%. We also had difficulty in getting gas free from carbon monoxide. By working the pump at its highest speed and reducing the amount of oil used to a minimum we reduced the carbon monoxide to 1.6 per cent. We were never bothered with oxygen as it never run higher than .5 to .7 per cent and usually there was none.

If this method of obtaining nitrogen be perfected it should supplant both other methods, to a large extent if not entirely. It affords a cheap means of obtaining the gas, without any great initial cost. The nitrogen could easily be obtained from the flue gases from power plants if

the firing was done carefully so as to avoid the formation of carbon monoxide. The method we used in the laboratory could easily be carried out on a commercial scale as the oil and lime are both very cheap. The greatest expense perhaps would be the lime, which owing to the excessive amount of carbon dioxide soon becomes saturated with this gas and new lime must be added.

The greatest weakness of this method of preparing nitrogen is the difficulty of obtaining a pure product. If too little oxygen enters with the oil there will be a percentage of carbon monoxide present which can not be washed out economically. If too much oxygen be admitted the excess will go through the system and remain in the nitrogen as an impurity. The last traces of carbon might be removed by putting another lime water scrubber in series with the others. The difficulty of changing the lime water so often could be done away with by having a continuous stream of

lime water flowing through the washer. In a small plant the flow could be very slow or even intermittent. Both the inlet and exhaust pipes should be near the bottom of the tank. The solution would have to be forced in under pressure and the exhaust pipe would have to rise high enough outside the tank to form a sufficient water seal to more than balance the internal pressure. There should not be a very large quantity of lime suspended in the water or the pipes would clog. To overcome the small supply of lime in the tank at any one time the flow of the solution should be increased. This would also help to keep the pipes open. This arrangement will do away with the difficulty of refilling the scrubbers at frequent intervals. If some arrangement can be made by which perfect combustion of some cheap fuel can be obtained this process for obtaining pure nitrogen will undoubtedly supplant the others.

REASONS FOR FAILURE.

In every case where we tried to make cyanamide we failed and the causes are about the same for every failure. In the experiments with the electric furnace the trouble lay in our failure to bring the nitrogen into intimate contact with the lime and carbon. Before the carbide was formed the nitrogen would not unite with the lime and carbon and when the carbide was formed it fused and ran to the bottom filling up the gas holes in the bottom. We found after a heat that all but one or two of the gas holes were filled with fused carbide and those that were open were greatly enlarged. The gas which came through those holes could nitrify the carbide next to it, but the great mass of the carbide never came in contact with the nitrogen at all. Instead of having a furnace like ours we should have had one so built that gas could come through a few holes at the bottom and sides and the pressure be great enough to prevent the fused carbide from stopping

the holes. Our furnace was open at all points and as soon as the gas entered the furnace it escaped at the easiest point which was usually near the bottom. Because of this only a small part of the solid matter came in contact with the gas. If the sides of the furnace were air tight then the nitrogen would be forced up through the mass and thus come in intimate contact with all of it. If a furnace could be made so that the entrance and exit of the gases could be controlled the nitrogen could be introduced under a pressure of about two atmospheres which would perhaps give a fair yield of cyanamide, for this pressure and the high temperature of the furnace ought to bring about a rapid absorption of the nitrogen.

When we used the bomb our greatest difficulties were the impurities in the gas, the poor mixing of the carbide and the nitrogen and the lack of sufficient pressure.

Reasons for Failure.

The action of the carbon monoxide forming a coating of lime and carbon has been previously explained. This coating of lime was formed as soon as the temperature of the furnace was high enough and always at the beginning of the heat. This coating was hard and enclosed the remaining carbide inside it so that the nitrogen could not come in contact with it. In the heats which were a failure from this cause not over 5% of carbon monoxide was present. This shows the harmful effect of a comparatively small amount of carbon monoxide.

The difficulty of obtaining an intimate mixture of the carbide and nitrogen was also a great drawback. We first tried the carbide pulverized. This formed too compact a mass and unless the bomb were continually shaken the mass caked. In this condition the gas could not permeate the mass and so absorption was very slow. Next we tried carbide which would pass a number 6 sieve, this gave some pieces which were too large

to be easily nitrified. The mass, however, did not cake. We found that the carbide which would pass a number 8 sieve and be retained by a number 10 sieve gave the best results. If we had had some arrangement to rotate the bomb during the heat the results would no doubt have been much better. Since we had no method of rotating the bomb continually we turned it every fifteen minutes.

Our last difficulty was due to lack of sufficient gas pressure. The gas was stored in a tank under a water seal. By placing weights on the top of the tank a pressure of two or three feet of water could be attained, but anything higher was impossible. Since the speed of absorption varies with the pressure the reaction was very slow. If we could have raised the pressure in our last heat to about two atmospheres we believe that we would have obtained a product with a fair percent of nitrogen. Before another set

of experiments are carried out an arrangement should be made whereby the gas in the tank could be pumped out and put under a high pressure in some receptacle which connects directly to a revolving bomb.

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